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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

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## TRANSMITTAL LETTER TO THE UNITED STATES

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DESIGNATED/ELECTED OFFICE (DO/EO/US)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

CONCERNING A FILING UNDER 35 U.S.C. 371

09/914204

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/GB00/00671

24 FEBRUARY 2000

26 FEBRUARY 1999

TITLE OF INVENTION

A METHOD OF PROCESSING A POLYMER LAYER

APPLICANT(S) FOR DO/EO/US

MACNEIL, John      WILBY, Anthony, Paul  
BEEKMAN, Knut

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

## Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

PCT WRITTEN OPINION (FORM PCT/IPEA/408)  
UNEXECUTED DECLARATION

09/912204

PCT/GB00/00671

WLJ.075

24. The following fees are submitted:

**BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :**

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . \$1000.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . \$860.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . \$710.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$690.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =****\$860.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

**\$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	19 - 20 =	0	x \$18.00
Independent claims	1 - 3 =	0	x \$80.00

**\$0.00****\$0.00**

Multiple Dependent Claims (check if applicable).

☐**\$0.00****TOTAL OF ABOVE CALCULATIONS =****\$860.00**

☐ Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

**\$0.00****SUBTOTAL =****\$860.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

**\$0.00****TOTAL NATIONAL FEE =****\$860.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☐**\$0.00****TOTAL FEES ENCLOSED =****\$860.00**Amount to be:  
refunded

\$

charged

\$

- a. ☒ A check in the amount of **\$860.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **50-0238**. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

ADAM C. VOLENTINE  
JONES VOLENTINE, P.L.L.C.  
12200 SUNRISE VALLEY DRIVE, SUITE 150  
RESTON, VA 20191

TEL. NO. (703) 715-0870

SIGNATURE

ADAM C. VOLENTINE

NAME

33289

REGISTRATION NUMBER

AUGUST 23, 2001

DATE

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of :  
John MACNEIL et al. : Attn: Applications Branch  
Serial No.: [NEW] : Attorney Docket No. WLJ.075  
Filed: August 23, 2001 :

For: A METHOD OF PROCESSING A POLYMER LAYER

**PRELIMINARY AMENDMENT**

Honorable Commissioner of  
Patents and Trademarks,  
Washington, D.C. 20231

Sir:

Preliminary to the examination of the above-identified application, please enter  
the following amendments and consider the following remarks:

**IN THE CLAIMS:**

Please amend claims 4, 6, 8, 10, 12, and 14-19 as follows (a marked-up version  
of the original claims is attached herewith):

4. (Amended) A method as claimed in Claim 1 where the layer is supported on  
an electrode and the plasma is at least partially maintained by an RF power source  
connected to the electrode.

6. (Amended) A method as claimed in claim 1 wherein the plasma is at least  
partially maintained by an RF power source feeding an electrode spaced from the  
layer.

8. (Amended) A method as claimed in Claim 1 wherein the plasma is at least partially maintained by an inductively coupled power source.

10. (Amended) A method as claimed in Claim 1 wherein the heating step lasts for between 2 and 4 minutes.

12. (Amended) A method as claimed in Claim 1 wherein the layer is supported as a platen heated between 350°C and 550°C.

14. (Amended) A method as claimed in Claim 1 wherein the dielectric constant of the processed layer is below 3.00.

15. (Amended) A method as claimed in Claim 1 wherein the layer is treated by the plasma to depth  $>3000\text{\AA}$ .

16. (Amended) A method as claimed in Claim 1 wherein the layer is treated by the plasma to a depth of  $<600\text{\AA}$ .

17. (Amended) A method as claimed in Claim 1, wherein the layer is an insulating layer on a semiconductor wafer.

18. (Amended) A method as claimed in Claim 1, wherein the processing method reduces cracking in the layer.

19. (Amended) A method as claimed in Claim 1, wherein the processing method improves the wet etch rate of the layer.

**REMARKS**

By this Preliminary Amendment, claims 4, 6, 8, 10, 12, and 14-19 have been amended to eliminate multiple dependent claims. Entry of this Preliminary Amendment is respectfully requested.

Respectfully submitted,

Jones Volentine, P.L.L.C.



Adam C. Volentine  
Registration No. 33289

12200 Sunrise Valley Drive, Suite 150  
Reston, VA 20191  
Tel. (703) 715-0870  
Fax (703) 715-0877

Date: August 23, 2001

## CLAIMS

1. A method of processing a polymer layer including Si-C bonds including the steps of heating the layer to desorb moisture and harden the layer and exposing the layer to a plasma during the heating process.
2. A method as claimed in Claim 1 wherein the plasma is a hydrogen plasma.
3. A method as claimed in Claim 1 wherein the plasma is present throughout the heating stage.
4. A method as claimed in <sup>Claim 1</sup> ~~any one of the preceding claims~~ where the layer is supported on an electrode and the plasma is at least partially maintained by an RF power source connected to the electrode.
5. A method as claimed in Claim 4 wherein the power source is between 400 and 750 watts.
6. A method as claimed in ~~any one of claims 1 to 3~~ wherein the plasma is at least partially maintained by an RF power source feeding an electrode spaced from the layer.
7. A method as claimed in Claim 6 wherein the power is supplied between 400 and 750 watts.
8. A method as claimed in ~~any one of Claims 1 to 5~~ wherein the plasma is at least partially maintained by an inductively coupled power source.

9. A method as claimed in Claim 8 wherein the power supplied is between 400 and 750 watts.

10. A method as claimed in <sup>Claim 1</sup> ~~any one of the preceding~~  
~~claims~~ wherein the heating step lasts for between 2  
5 and 4 minutes.

11. A method as claimed in Claim 10 wherein the heating step lasts for 3 minutes.

12. A method as claimed in <sup>Claim 1</sup> ~~any one of the preceding~~  
~~claims~~ wherein the layer is supported as a platen  
10 heated to between 350°C and 500°C.

13. A method as claimed in Claim 1 wherein:

(1) the plasma is maintained by an RF power source connected to a platen on which the layer is supported and the power source provides  
15 substantially 600 watts;

(2) the plasma is a hydrogen plasma;

(3) the platen is heated to between 400°C and 500°C;  
and

(4) the heating step lasts for substantially 3  
20 minutes.

14. A method as claimed in <sup>Claim 1</sup> ~~any one of the preceding~~  
~~claims~~ wherein the dielectric constant of the  
processed layer is below 3.00.

20

Claim 1

15. A method as claimed in ~~any one of the preceding~~  
claims wherein the layer is treated by the plasma to  
a depth  $>3000\text{\AA}$ .
16. A method as claimed in ~~any one of the preceding~~  
5 ~~claims~~ <sup>Claim 1</sup> wherein the layer is treated by the plasma to  
a depth of  $<600\text{\AA}$ .
17. A method as claimed in ~~any one of the preceding~~  
10 ~~claims~~ <sup>Claim 1</sup> wherein the layer is an insulating layer on a  
semiconductor wafer.
18. A method as claimed in ~~any one of the preceding~~  
15 ~~claims~~ <sup>Claim 1</sup> wherein the processing method reduces cracking  
in the layer.
19. A method as claimed in ~~any one of the preceding~~  
20 ~~claims~~ <sup>Claim 1</sup> wherein the processing method improves the wet  
etch rate of the layer.



A Method of Processing a Polymer Layer

This invention relates to a method of processing a polymer layer, such as a short chain polymer layer, including Si-C bonds and in particular for processing low dielectric constant films of the type, for example, that are used as insulating layers on semiconductor wafers.

The pressure to produce semiconductor wafers with high device densities and high speeds has led to a search for low dielectric constant films for use as insulating layers in semiconductor devices. Such layers can be either spun on or deposited using, for example, chemical vapour deposition process. The layer is then usually heated to harden it. Recent work has been particularly directed to films consisting of polymer layers including Si-C bonds and the Applicants' International Patent Application WO 98/08249 describes, by way of example, such a process for depositing such a film.

The reduction in dielectric constant in such films seems to derive from a decreased density of film, possibly due to a disruption of the lattice by the carbon atoms present in the film.

The dielectric material forms or is deposited upon the wafer as a short chain polymer that is further polymerised and hardened by heating to between 400° and

500°C, typically in a nitrogen atmosphere of between 30 mTorr and 20 Torr and more generally in the absence of oxygen at any convenient pressure.

It has become apparent, however, that at least some films of this sort are susceptible to cracking, particularly at the wafer edge and an illustration of this is shown in Figure 1. Typically such cracking begins to occur at a nominal film thickness of about 5000-6000 Å. The cause seems in part to be due to a dramatic increase in film thickness within 1mm of the wafer edge. Figure 2 shows the profile in this respect. The cracking appears only to occur following exposure to atmosphere and aggressively travels in towards the centre over a period of about 24 hours. The rate of cracking can be delayed by keeping the wafers in vacuum, but eventually they do crack when exposed to atmosphere.

The present invention consists in a method of processing a polymer layer including Si-C bonds including the steps of heating the layer to desorb moisture and harden the layer and exposing the layer to a plasma during the heating process.

Usually the deposited polymer layer comprising a short chain polymer, the heating further polymerising the layer.

It is particularly preferred that the plasma is a hydrogen plasma, but it is believed that a plasma based on oxygen getters may be particularly appropriate. It is preferred that the plasma is present throughout the heating stage.

The plasma may be maintained by the wafer support RF driven electrode on which the layer is supported e.g. indirectly on a semiconductor wafer reactor electrode (sometimes known as Reactive Ion Etch (RIE) mode even if no etching occurs); by a capacitively coupled RF electrode spaced from the wafer (often referred to as a "diode configuration"; or by an inductively coupled arrangement (typically known as inductively coupled plasma (ICP)). In addition a combination of ICP and RIE can be run. In any of these cases, for the purposes of this invention, the power supplied to the plasma may be of the order of between 400 and 750 watts the RF power required depending in part at what temperature the treatment of the layer takes place. Thus usually the wafer will be supported on a platen heated to a temperature of the order of between 350°C and 500°C.

In a particularly preferred arrangement the method has the following characteristics:

(1) The plasma is maintained by an RF power source connected to a platen on which the wafer is supported and the power supply provides substantially 600 watts.

(2) The plasma is a hydrogen plasma;

(3) The platen is heated to between 400°C and 500°C; and

(4) The heating step lasts for substantially 3 minutes.

In any of the above methods the dielectric constant of the processed layer is preferably below 3.

The layer may typically be an insulating layer on the semiconductor wafer.

It has now been established that further surprising benefits can be obtained if low k films are treated in this manner and these are set out below:

Although the invention has been defined above, it is to be understood it includes any inventive combination of the features set out above or in the following description.

The invention may be performed in various ways and a specific embodiment will now be described by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a micrograph taken by an optical microscope of the edge of a wafer showing cracking of the layer after exposure to atmosphere, the layer having been processed in the prior art manner;

5 Figure 2 is a graph demonstrating the thickness profile of a low k film;

Figure 3 illustrates k values resulting from various experiments;

10 Figure 4 is an equivalent graph for further process conditions;

Figure 5 shows Fourier Transform Infra Red (FTIR) data gathered from a central sample;

Figure 6 shows FTIR data for a sample prepared in accordance with an embodiment of the invention;

15 Figure 7 and 8 plot dielectric constant against plasma heating time at various temperatures and generally correspond with Figure 4; and

20 Figures 9 to 12 illustrate the effect of strip process on k-value; and Figure 13 indicates k value stability.

Experiments were run to monitor both cracking and k (dielectric constant) values. Each property was also checked with time. The k values were measured on low resistivity silicon MOS structures and the cracking was

monitored by optical microscope inspection under dark field illumination.

The deposition of the low k film onto silicon wafers was carried out in a standard chemical vapour deposition process with the following characteristics:

Methyl silane flow	100 sccm
Hydrogen peroxide	0.5 g/min
Pressure	1000 mTorr
Platen temperature	2°C
Showerhead temperature	100°C

As a first step, the thus deposited short-chain polymer layer was then subjected to the standard heat treatment, but this time with a coincident plasma. Various plasma treatments including hydrogen, argon, nitrogen, nitrous oxide and oxygen were run. Some benefit on cracking was observed which encouraged further experiments combining higher temperatures of heat treatment with various configurations of applied plasma power.

As has been discussed above, these plasma modes comprise the following:

- (1) RIE
- (2) Diode
- (3) ICP
- (4) ICP and RIE in combination.

Initially, hydrogen plasmas were run in RIE and ICP, both separately and combined, at temperatures of 400°C, 450°C and 500°C for three minutes and these were compared to an argon run in diode mode at 400°C.

5 The results of these experiments show that a reduction in cracking could be achieved and therefore further trials were carried out at higher temperatures in diode mode.

10 These further experiments used a hydrogen plasma with a nominal platen temperature of 500°C using a 13.56MHz power supply although, in the absence of the plasma, the wafer temperature is estimated to reach approximately 375°C due to poor thermal coupling at low pressures and in the absence of wafer clamping. Wafer temperatures whilst  
15 a plasma is running, would be expected to be higher. Difficulties were experienced in obtaining meaningful experimental measurements of actual wafer temperatures due to RF interference on thermocouples.

20 The typical process conditions using a hydrogen plasma were as follows:

**Diode mode**

R.F. Power	1000 W
R.F. Frequency	13.56 MHz
Hydrogen flow	1000 sccm
Pressure	4 Torr
Platen Temperature	500°C (Wafer temperature unknown but >375°C)

Spacing	10mm
Time	180 seconds

## ICP and RIE modes:

	ICP mode	RIE mode'	ICP+RIE
R.F.Power ICP	500W	-	-
R.F.Power Platen	-	600W	-
R.F.Power ICP/Platen	-	-	500/250
Pressure	4m Torr	450 mTorr	4 Torr
Platen Temperature	400-500°C	350-500°C	400-500°C
Time	60-300 secs	60-300 secs	60-300secs

The preferred process was run at 350°C or 400°C for three minutes. Argon was also used but hydrogen was preferred. Hydrogen produced DC bias levels of 475V against 260V with argon.

In addition control experiments were run using a typical heat only process and the two conditions used are set out below.

	Step 1	Step 2
Platen temperature (wafer temperature)	500°C (~150°C)	500°C (~460°C)
Pressure	30 mTorr	10 Torr
Time	60 seconds	300 seconds

The results of many of these experiments are illustrated in Figure 3. This shows the k value obtained for various process temperatures, excitation modes and time periods. That for the 500° temperature/ICP and RIE combined may show a measurement error, but alternatively it may be indicative of some irreversible change taking place if the film exceeds a critical temperature.



Each result represents a single experiment and a subsequent k value measurement.

Crack tests were carried out on approximately 7,000 Å films. The RIE only treatments showed no cracking, whilst the controls (heat treatment only) cracked to 25mm from the edge of the wafer. There was minimal cracking up to approximately 0.25mm from the edge of the ICP and combined ICP and RIE treatments, although there was no significant trend with platen temperatures in the range 400°C to 500°C. The RIE alone process also achieved particularly desirable k values and so, from the work done to date, this would appear to be the preferred process although the higher k values may be acceptable for many wafer configurations.

Figure 4 shows a further experiment using RIE modes of treatment mainly for hydrogen plasmas but with variations in the time and temperature combinations. The third pair of points from the right were obtained with an argon plasma. The controls were prepared as before. The measurement bars for the k values indicate that obtained shortly after treatment and that obtained 48 hours after the treatment.

The degree of cracking was worse for argon and for the 350°C/60s treatment. These experiments showed cracking extending approximately 0.33mm in from the wafer

edge for approximately 7000 Å film, but it will be appreciated that these results are still noticeably better than for heat treatment alone. The other results showed cracking was not seen until almost 9000 Å film thickness occurred and the best process seems to lie for a film between 8000 and 9000 Å. Note that these are nominal layer thicknesses across the majority of the wafer. Cracking takes place in a part of the layer much thicker than this nominal thickness e.g. at the edge of the wafer as illustrated in Figure 2.

Some further experiments have been run in diode mode which suggests that comparable benefits to RIE can be obtained, but the plasmas were run at a much higher pressure (4 Torr) and much higher powers (1000 watts). This may significantly affect the wafer temperature and consideration may have to be given to the question of thermal budget.

Figure 5 shows FTIR data gathered with the control process whilst Figure 6 shows similar data from a hydrogen plasma diode mode. The heat only proves results in a final wafer temperature of approximately 460°C the wafer temperature of the hydrogen plasma treated wafer is not definitely known but must be greater than 375°C as this is the wafer temperature achieved without plasma (all other

process conditions remaining the same). It is thus clear that the hydrogen plasma treatment may result in a different wafer temperature to that of the prior art process of the control and thus affects the layer treatment. It is also believed that the plasma acts upon the layer not simply as a heat source. There are obvious differences resulting from the hydrogen plasma treatment. Figure 6 shows reduced C-H, Si-H, Si-CH<sub>3</sub> and Si-O(Si<sub>2</sub>O<sub>3</sub>) peaks. From previous experience the Applicants would have expected that such a variation would have yielded higher k values however the k values of the two examples shown are 2.84 and 2.77 respectively.

The following table shows the results of the k values and cracking distances for diode mode plasma treatment as set out above.

Treatment Temperature	Thickness after treatment	K value after treatment	K value after 24 hours	Cracking (distance from edge)
200	8819	2.86	3.05	5.00 mm
300	8382	-	-	2.00 mm
400	7871	2.76	2.79	0.75 mm
500	7731	2.76	2.77	None

Thus the hydrogen plasma treatment significantly changes the film structure, as shown by the FTIR. Whilst it is difficult to reconcile these changes with the fact that the k value remains low, this reduction in carbon and hydrogen content may make these films more convenient for

use in semiconductor manufacture. The process is thus of value not simply to avoid the cracking of thick (greater than 7000-Å) polymer layers containing Si-C bonds.

It will be again seen from Figures 7 and 8, that combination of heat and plasma exposure time affect the k-value achieved for example a 3 minute plasma exposure at 350°C or a 2 minute exposure at 400°C appear particularly efficacious.

Looking at the benefits of the treated films the wet etch rate of hydrogen treated films using a 10:1 BOE (buffered oxide etch) at 20°C are typically similar to or less than that of thermal oxide i.e. around 550 Å/min. The untreated films etch at over 10,000 Å/min. Accordingly the hydrogen plasma treatment therefore reduces the wet etch rate by a factor of 20 or more. Wet etch rate is generally used as an indication of merit for silicon dioxide layers where thermal oxide is considered to be of high quality.

It has been determined that hydrogen plasma treatment is effective to varying depths dependent on the time of the process and the composition of the film. In general the lower the k value the greater the depth of treatment. Thus for a k=2.7 film, the treatment penetrated to a depth of 3,000 Å whilst with a k=2.4 film the depth of treatment

was 5,700 Å. Both tests were carried out under the following conditions:

Hydrogen Flow	1000 sccm
Platen Temperature	400°C
RF Power	1000 Watts
RF Frequency	13.56 MHz
Pressure	4 Torr
Electrode Spacing	6mm
Time	300 seconds

It has been found that increasing the power level or changing the electrode spacing does not significantly increase the effective depth of the plasma treatment, but increasing the treatment time to 600 seconds increases the depth of treatment on the  $k=2.7$  film from 3000 Å to 6000 Å. (i.e. twice the time, twice the depth).

It will have been noted from our earlier application that the hydrogen treatment also improves, i.e. lowers, the  $k$  value. It was considered desirable to determine whether this  $k$  value improvement could be achieved for the bulk of the material, even if only a surface treatment took place. Accordingly a 6000 Å,  $k=2.7$  film was formed first by depositing two 3000 Å layers, each of which were treated with a hydrogen plasma for 300 seconds. Secondly 6000 Å layers were deposited and treated for either 300 or 600 seconds. No variation in  $k$  value was determined. This appears to show that the film that was only treated

to half its depth is still yielding an improved k value of the previous best known method of a vacuum thermal process, which is presumed to give a bulk effect. It is thus postulated that the hydrogen plasma is effective at reducing k values even as a surface treatment perhaps by reducing the likelihood of water re-absorption whilst the applied heat may be a bulk effect performing the bulk moisture desorption from the as-deposited layer. The hydrogen plasma clearly changes the bonding composition as evidenced by the FTIR data yielding an as-treated layer that etches slower and providing a treated layer that protects the underlying part of the layer from subsequent plasma etch processes and presumably water re-absorption. Thus the hydrogen plasma is effective on a heated layer at improving at least a surface of that layer to the benefit of the whole layer, the improvement being an improvement in the layers usefulness as a low k dielectric in a semiconductor device.

It had previously been found that if the low k films were subjected to oxygen based resist stripping process necessary if low k films are to be integrated into subtractive and damascene schemes using standard processes then carbon tended to be stripped out of the films and

presumably replaced by water accompanied by a substantial increase in the k value.

Although Figures 5 and 6 indicate that the C-H and SiH bonds are reduced by the hydrogen plasma, resultant structure appears to be stable under strip process.

Thus turning to Figures 9 to 12 the integrated peak area ratios for the various indicated bonds are not changed substantially by an oxygen based stripping process. Similarly the effects of the oxygen and hydrogen (reducing) resist strips are shown on the hydrogen plasma treated films refractive indexes in Figures 11 and 12. Refractive index is an indirect indication of k value.

The hydrogen plasma treatment is thus shown to provide an effective barrier to a subsequent oxygen-based plasma process.

In order to ascertain the stability of the k value wafers were blanket coated in a k=2.7 Si-C polymer and were then subjected to a standard fluorine based dielectric etch process, followed by a hydrogen plasma (reducing) resist strip process to simulate conditions on the exposed parts of a patterned etched dielectric structure. The dielectric constant was shown (see Figure 13) to remain at 2.7 after these etch and strip processes and to be stable over time. After 48 hours the k value

had increased slightly. A 450°C anneal brought the k value back down to 2.7 and after a further 48 hours the k value had increased only very slightly.

5 The improvement in the surface layer of the low k dielectrics such that its wet etch rate equates to that of a thermal oxide may be particularly advantageous in connection with chemical mechanical polishing. The mechanical/chemical abrasion of low k dielectrics of the nano-porous and/or carbon containing kind presents a  
10 problem as they are typically of low density and have poor mechanical strength. Attempts to chemical mechanical polish such layers tends to cause dishing of the dielectric between the areas of metalisation. This should be less apparent with low k films which have been treated  
15 according to the invention.

The advantage of using a hydrogen plasma on a heated wafer were also recognised in our co-pending application U.K. No. 99044273 (now PCT Application No. ) which  
20 is incorporated herein by reference. This in particular indicates that hydrogen mixed with etch gas may maintain or enhance the low k structure during etching. It would therefore be particularly advantageous to use that approach when etching materials prepared in accordance with this application.



It has also been appreciated that if the surface of the low k material is treated as described, then it will be possible in at least certain cases to dispense with the capping layer that has been used to date and thus compensate for the rather long cycle times which were mentioned in 9904427.3.

## CLAIMS

1. A method of processing a polymer layer including Si-C bonds including the steps of heating the layer to desorb moisture and harden the layer and exposing the layer to a plasma during the heating process.
2. A method as claimed in Claim 1 wherein the plasma is a hydrogen plasma.
3. A method as claimed in Claim 1 wherein the plasma is present throughout the heating stage.
4. A method as claimed in any one of the preceding claims where the layer is supported on an electrode and the plasma is at least partially maintained by an RF power source connected to the electrode.
5. A method as claimed in Claim 4 wherein the power source is between 400 and 750 watts.
6. A method as claimed in any one of claims 1 to 3 wherein the plasma is at least partially maintained by an RF power source feeding an electrode spaced from the layer.
7. A method as claimed in Claim 6 wherein the power is supplied between 400 and 750 watts.
8. A method as claimed in any one of Claims 1 to 5 wherein the plasma is at least partially maintained by an inductively coupled power source.

9. A method as claimed in Claim 8 wherein the power supplied is between 400 and 750 watts.
10. A method as claimed in any one of the preceding claims wherein the heating step lasts for between 2 and 4 minutes.
11. A method as claimed in Claim 10 wherein the heating step lasts for 3 minutes.
12. A method as claimed in any one of the preceding claims wherein the layer is supported as a platen heated to between 350°C and 500°C.
13. A method as claimed in Claim 1 wherein:
- (1) the plasma is maintained by an RF power source connected to a platen on which the layer is supported and the power source provides substantially 600 watts;
  - (2) the plasma is a hydrogen plasma;
  - (3) the platen is heated to between 400°C and 500°C; and
  - (4) the heating step lasts for substantially 3 minutes.
14. A method as claimed in any one of the preceding claims wherein the dielectric constant of the processed layer is below 3.00.

15. A method as claimed in any one of the preceding claims wherein the layer is treated by the plasma to a depth  $>3000\text{\AA}$ .
16. A method as claimed in any one of the preceding claims wherein the layer is treated by the plasma to a depth of  $<600\text{\AA}$ .
17. A method as claimed in any one of the preceding claims wherein the layer is an insulating layer on a semiconductor wafer.
18. A method as claimed in any one of the preceding claims wherein the processing method reduces cracking in the layer.
19. A method as claimed in any one of the preceding claims wherein the processing method improves the wet etch rate of the layer.

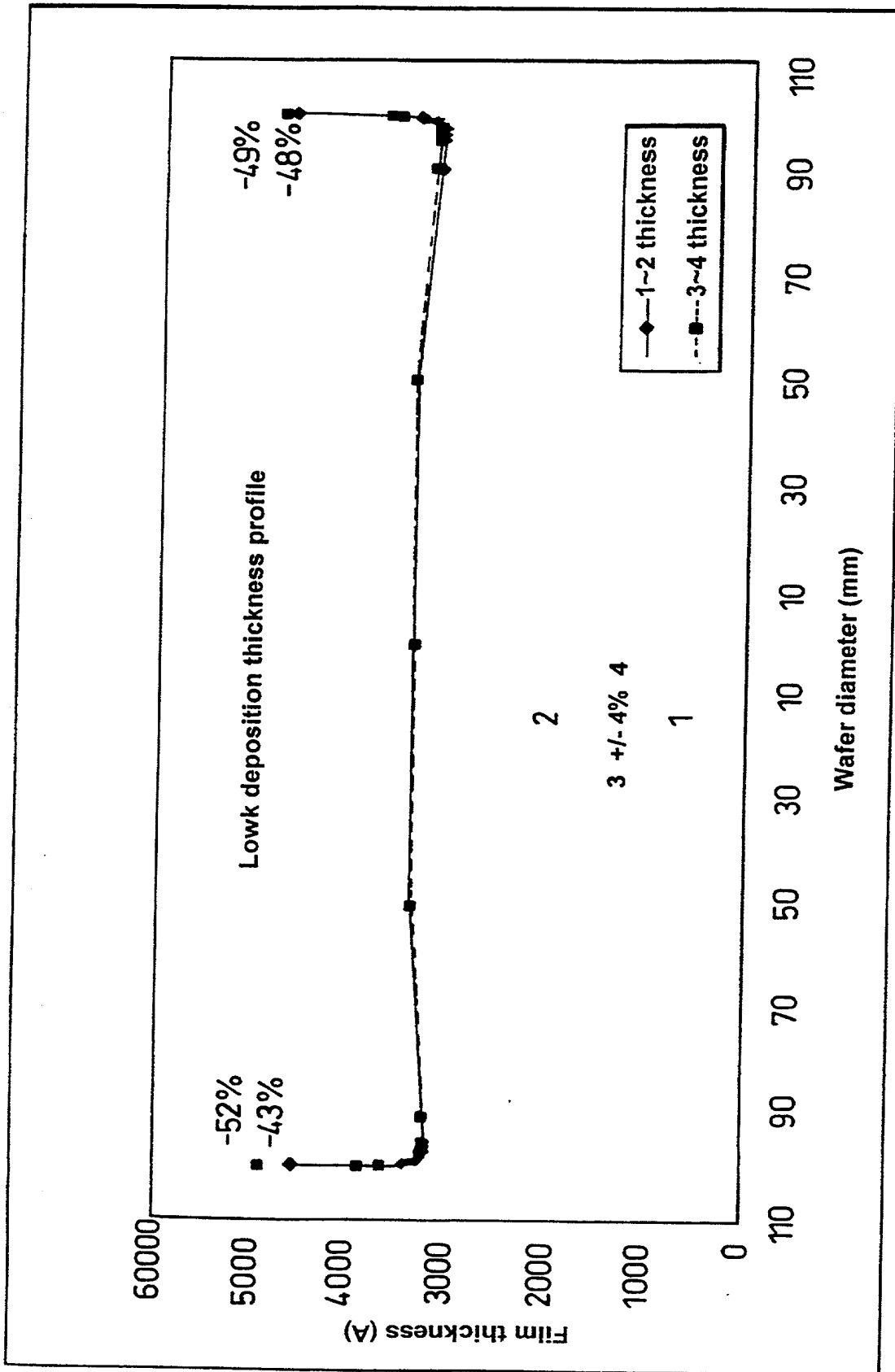
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Edge cracking as seen by optical microscope under dark field illumination

*Fig. 1*

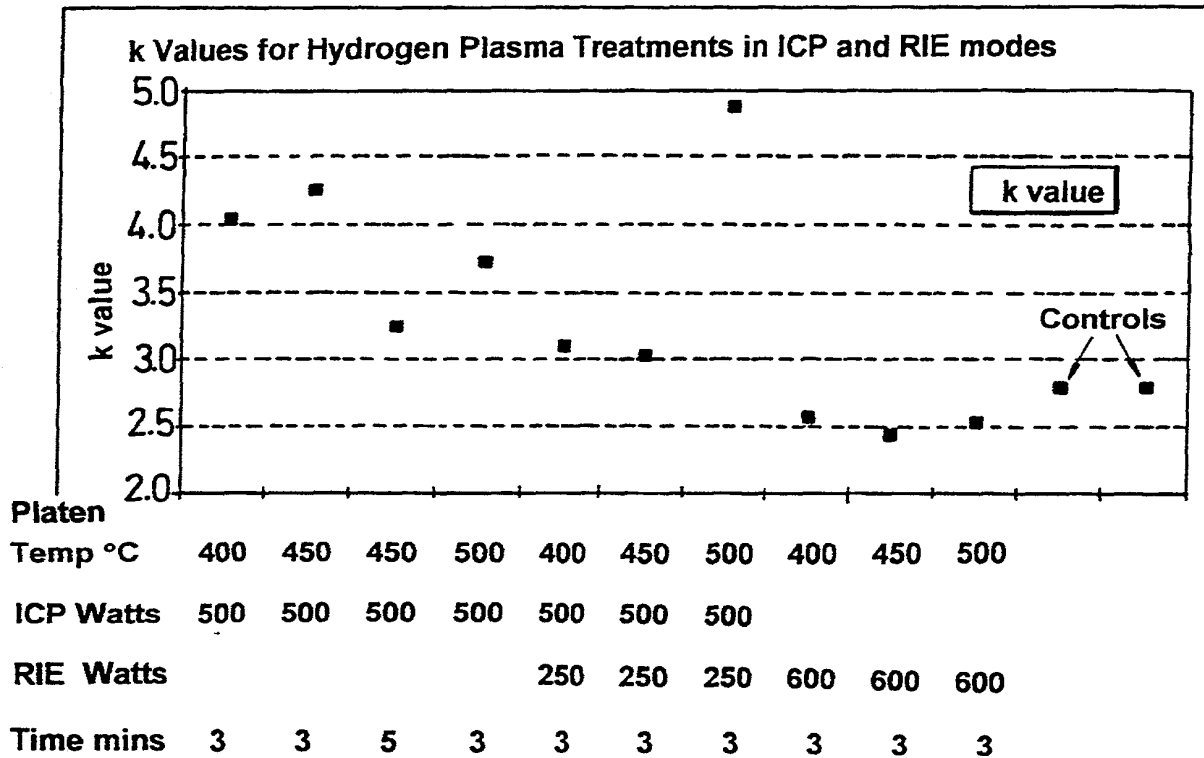
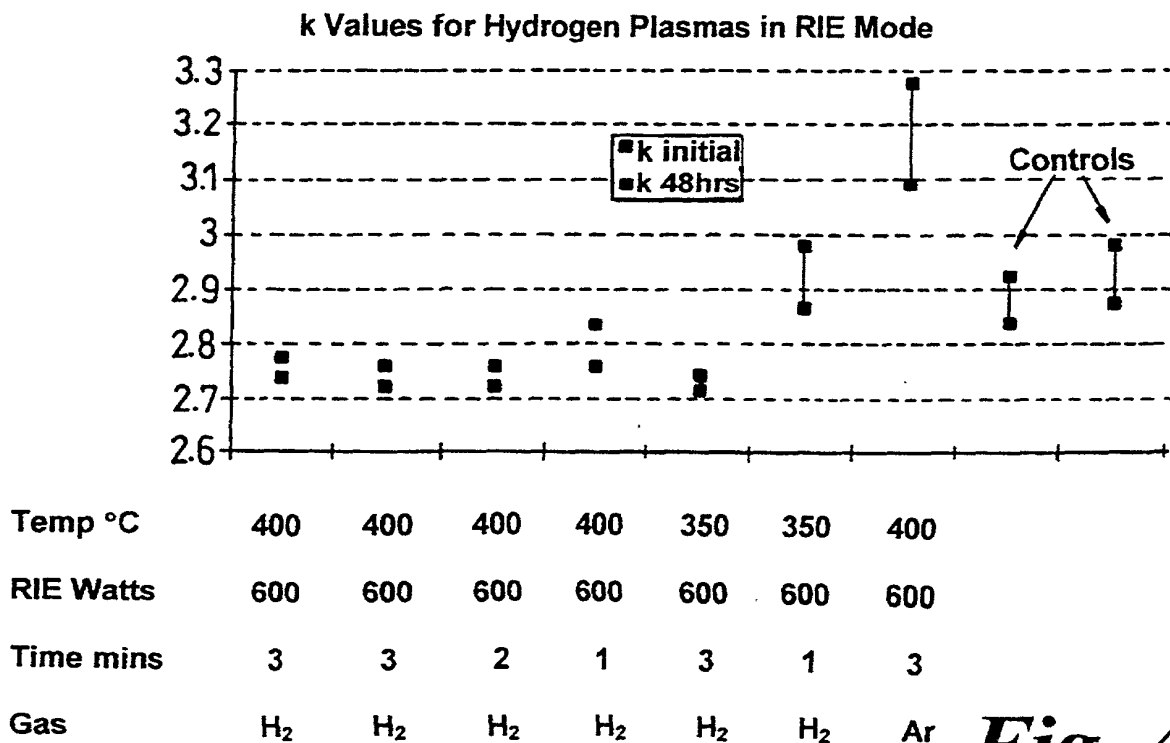
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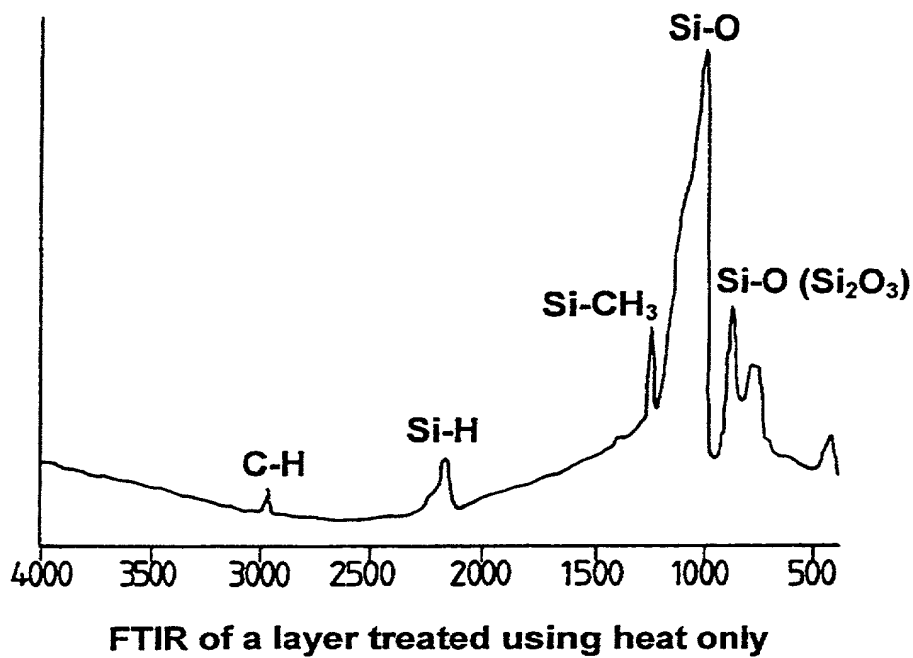
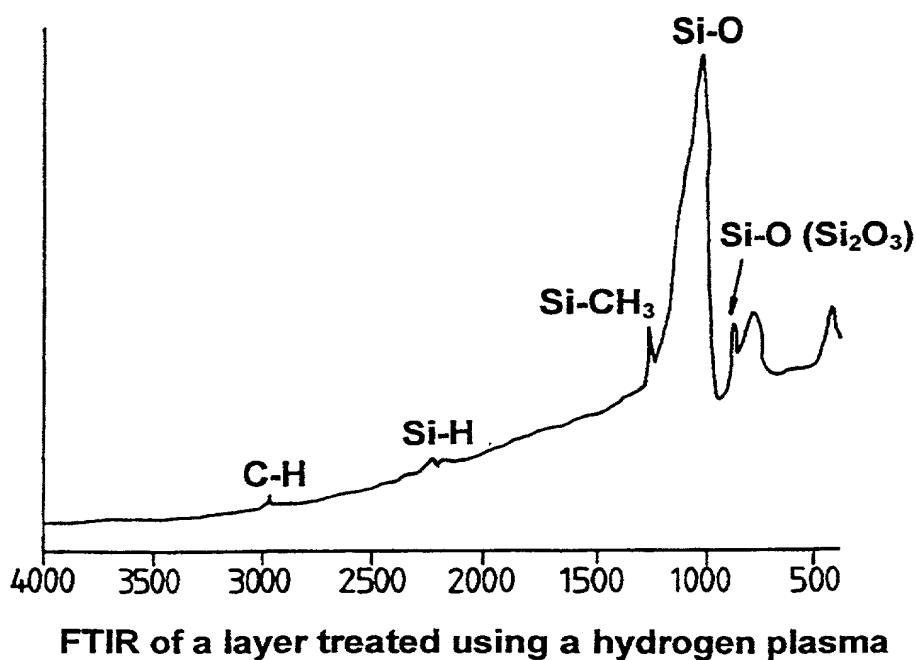
Low k film thickness profile to wafer edge

Fig. 2

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*Fig. 3**Fig. 4*

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*Fig. 5**Fig. 6*



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Dielectric Constant vs Hydrogen Plasma Treatment Time

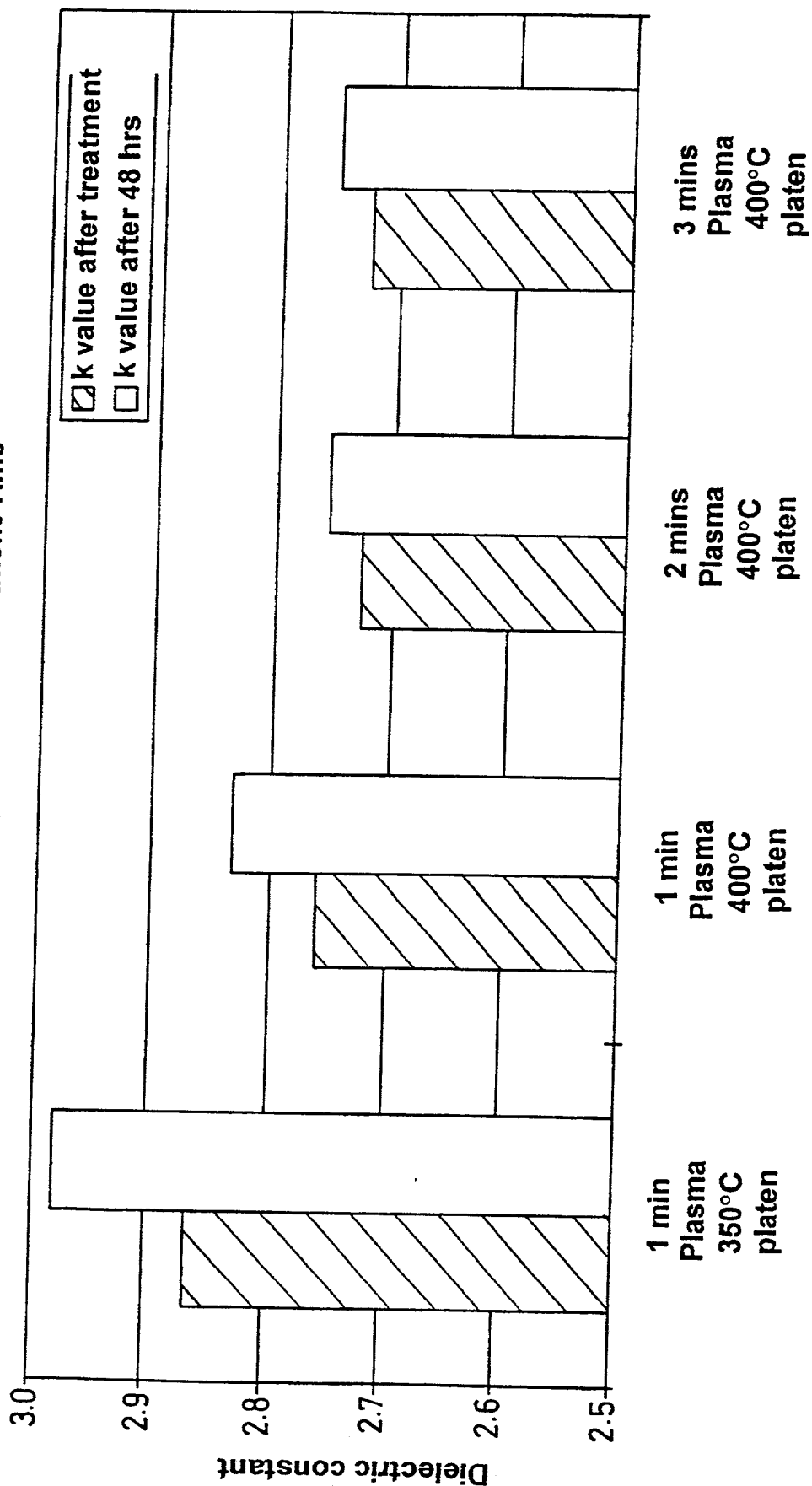


Fig. 7

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Dielectric Constant vs Hydrogen Plasma Treatment Temperature

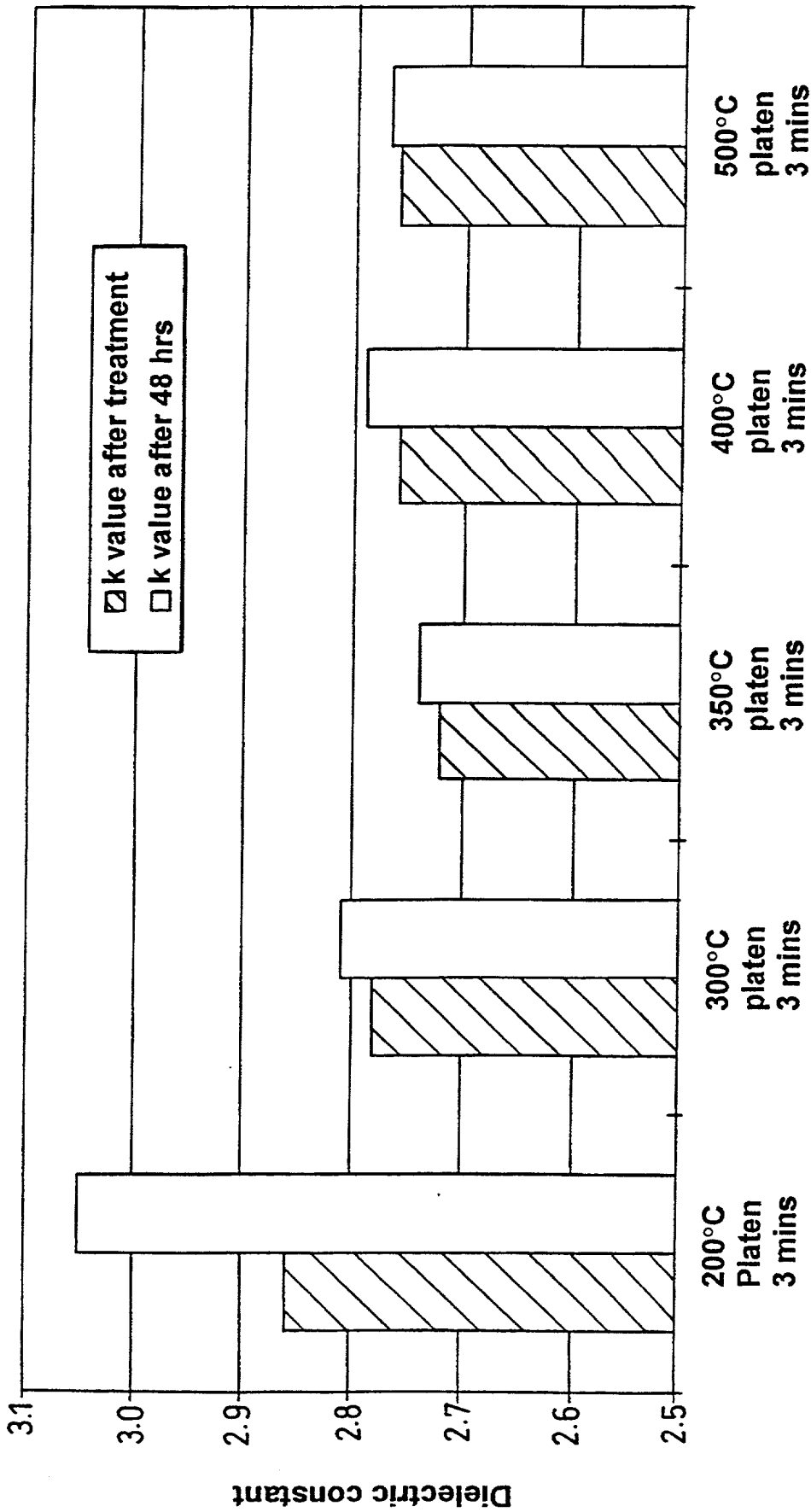
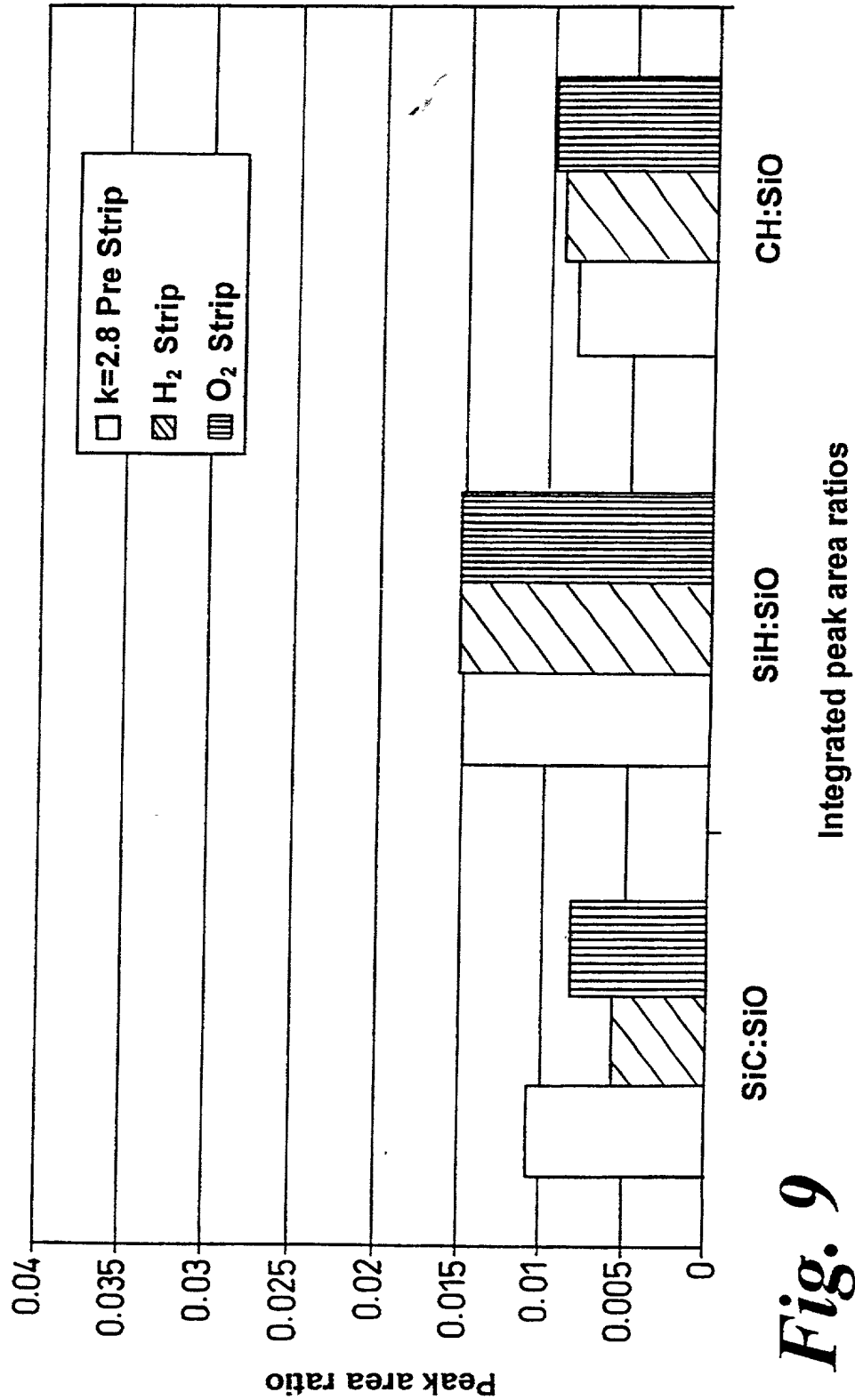


Fig. 8

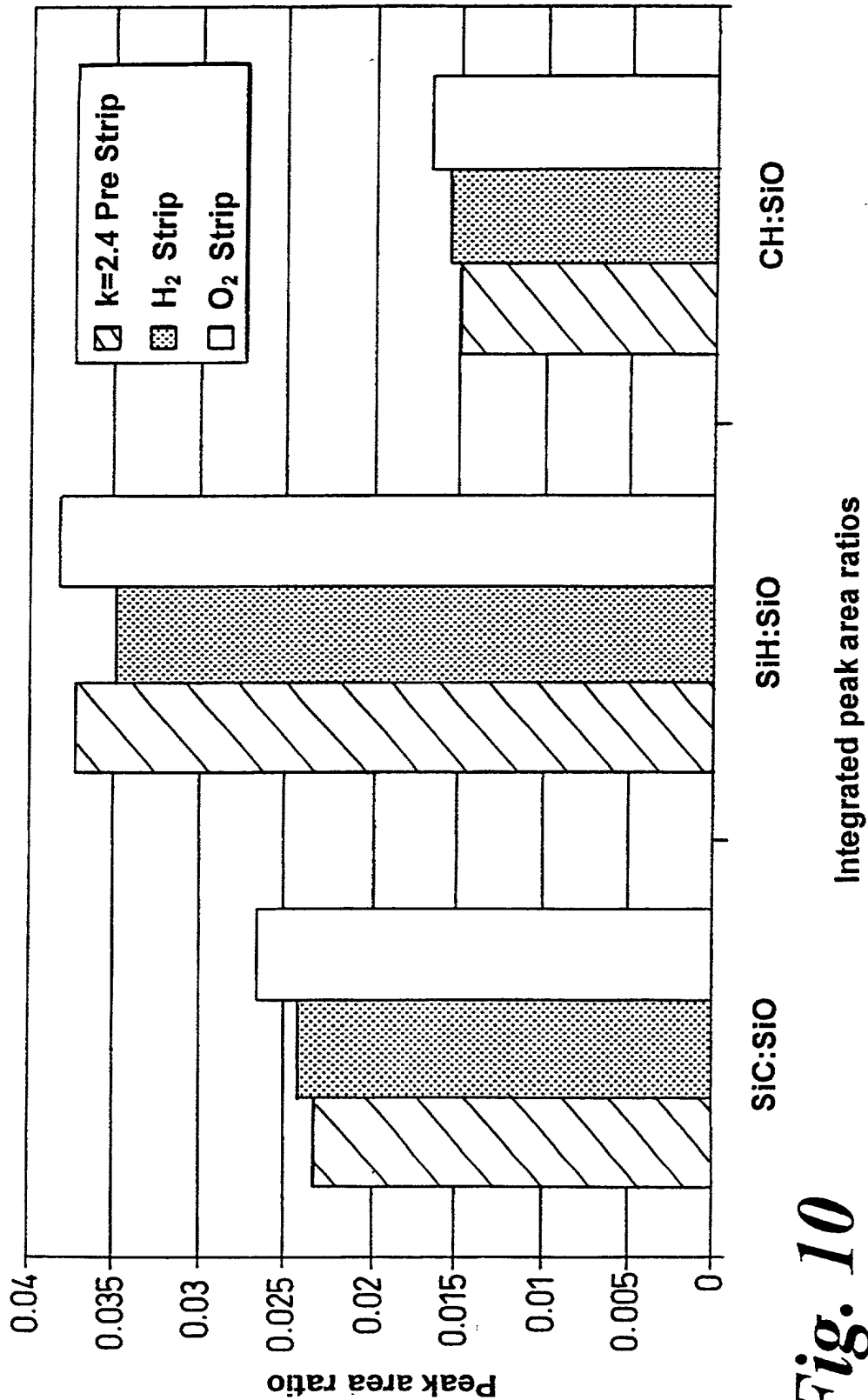
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Effect of hydrogen and oxygen strip on Flowfill (k=2.8) treated  
with H<sub>2</sub> plasma

**Fig. 9**

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Effect of hydrogen and oxygen strip on Flowfill (k=2.4) treated  
with H<sub>2</sub> plasma



**Fig. 10**

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Effect of hydrogen and oxygen strip on Flowfill (k=2.8) treated  
with H<sub>2</sub> plasma

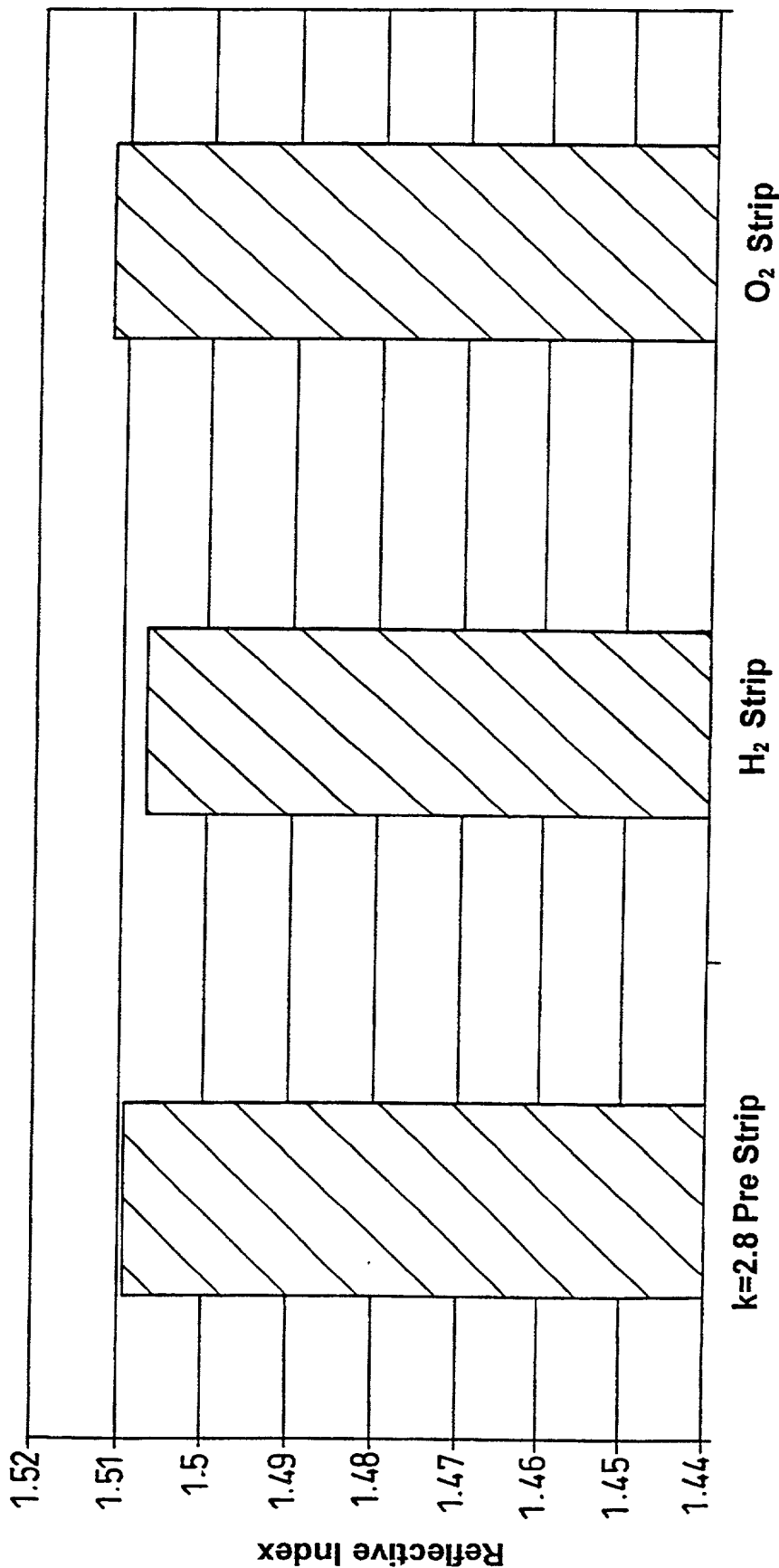


Fig. 11

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Effect of hydrogen and oxygen strip on Flowfill (k=2.4) treated  
with H<sub>2</sub> plasma

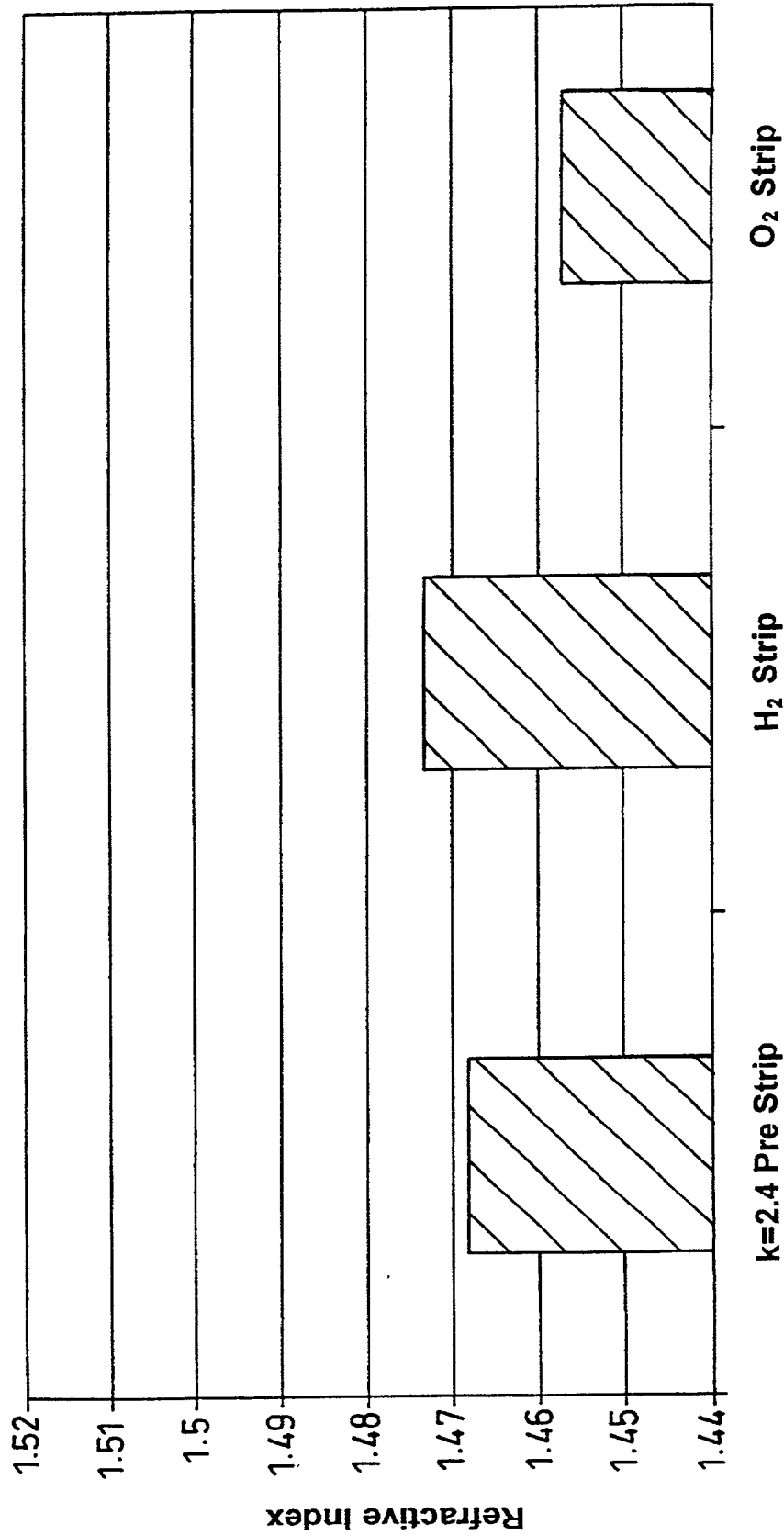
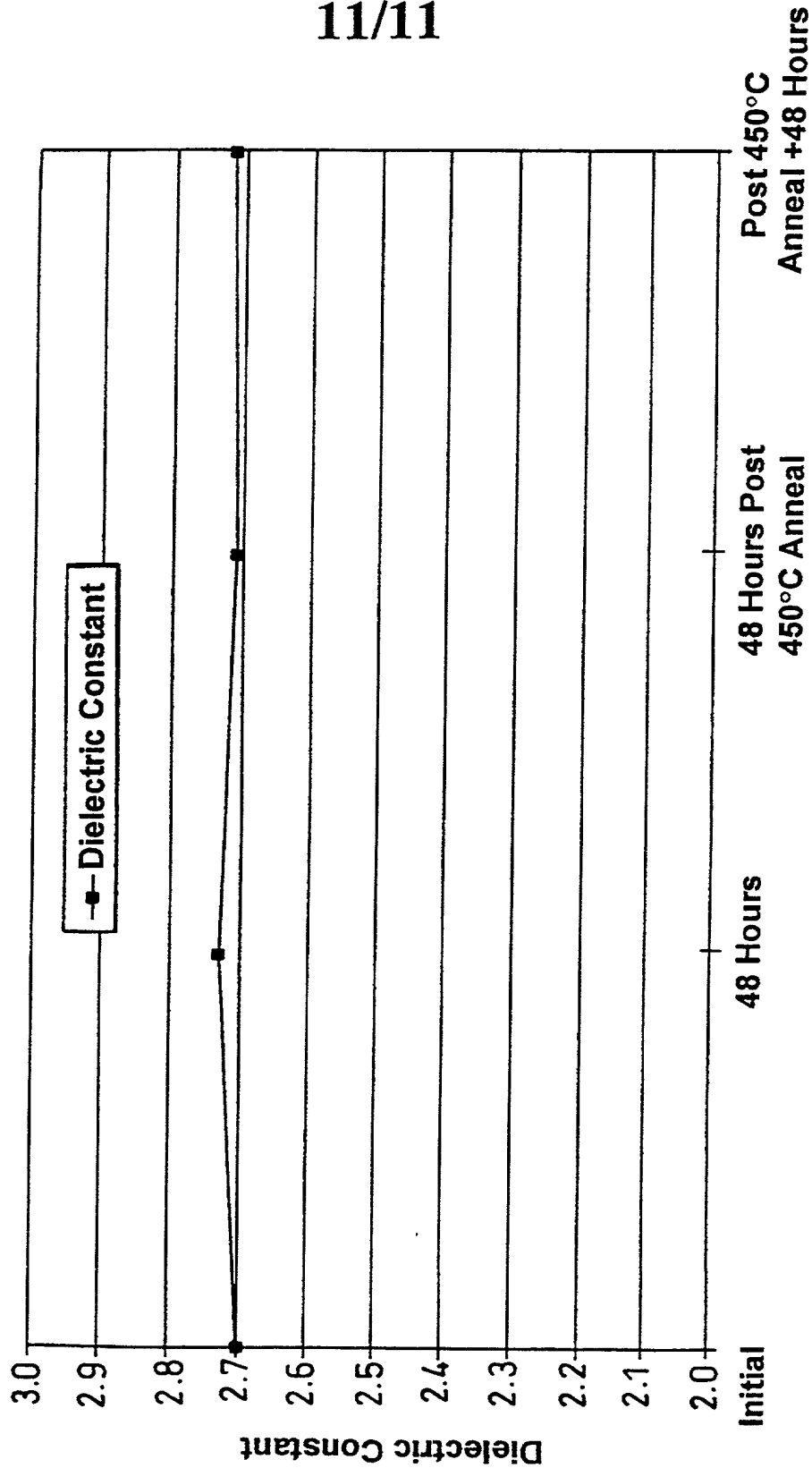


Fig. 12

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**Dielectric Constant Stability Post Reducing Strip Process  
90 Second Strip on Blanket Film With No Resist**

*Fig. 13*

VALENTINE FRANCOIS, P.L.L.C. (9/2001)

## DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

(X) Original ( ) Supplemental ( ) Substitute ( ) PCT ( ) Design

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

TITLE: A METHOD OF PROCESSING A POLYMER LAYER

of which is described and claimed in:

( ) the attached specification. *or*

( ) the specification in the application Serial No. \_\_\_\_\_ filed \_\_\_\_\_,  
and with amendments through \_\_\_\_\_ (if applicable), *or*

(X) the specification in International Application No. PCT/GB00/00671, filed 24 FEBRUARY 2000,  
and as amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose information of which I am aware which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
GREAT BRITAIN	9904427.3	26 FEBRUARY 1999	X
GREAT BRITAIN	9923801.7	28 SEPTEMBER 1999	X
GREAT BRITAIN	0000780.7	14 JANUARY 2000	X

I hereby claim the benefit under Title 35, United States Code, §120 and §119(e) of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:



APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

2 And I hereby appoint Adam C. Volentine, Reg. No. 33,289 and William S. Francos, Reg. No. 38,456, and the firm of VOLENTINE FRANCOS, P.L.L.C., jointly and severally, attorneys to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys named herein to accept and follow instructions from WYNN-JONES LAINE & JAMES as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

Kindly direct all correspondence to:

**VOLENTINE FRANCOS, P.L.L.C.**  
12200 Sunrise Valley Drive  
Suite 150  
Reston, Virginia 20191  
Telephone (703) 715-0870

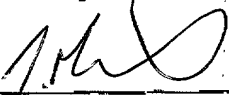
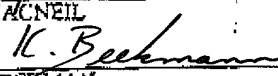
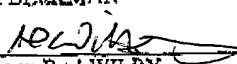
Full Name of 1st Inventor	FAMILY NAME <u>MACNEIL</u>	FIRST GIVEN NAME <u>John</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Heath</u> <u>GBN</u>	STATE OR COUNTRY <u>Great Britain</u>	COUNTRY OF CITIZENSHIP <u>Great Britain</u>
Post Office Address	ADDRESS <u>254 Heathwood Road, Heath, Cardiff CF4 4BS, Great Britain</u>		
Full Name of 2nd Inventor	FAMILY NAME <u>BEEKMAN</u>	FIRST GIVEN NAME <u>Knut</u>	SECOND GIVEN NAME
Residence & Citizenship	CITY <u>Yatton</u> <u>GBN</u>	STATE OR COUNTRY <u>Great Britain</u>	COUNTRY OF CITIZENSHIP <u>Great Britain</u>
Post Office Address	ADDRESS <u>18 Meadowland, Yatton, North Somerset BS49 4JB, Great Britain</u>		
Full Name of 3rd Inventor	FAMILY NAME <u>WILBY</u>	FIRST GIVEN NAME <u>Anthony</u>	SECOND GIVEN NAME <u>Paul</u>
Residence & Citizenship	CITY <u>Yate</u> <u>GBN</u>	STATE OR COUNTRY <u>Great Britain</u>	COUNTRY OF CITIZENSHIP <u>Great Britain</u>
Post Office Address	ADDRESS <u>55 Hay Leaze, Yate, Bristol BS37 7YJ, Great Britain</u>		

Full Name of 4th Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY ZIP CODE

Full Name of 5th Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY ZIP CODE

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor  Date 8/2/02  
John MACNEIL  
2nd Inventor  Date 12/2/02  
Knut BECKMAN  
3rd Inventor  Date 12/2/02  
Anthony Paul WILBY  
4th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
5th Inventor \_\_\_\_\_ Date \_\_\_\_\_

\*\*\*\*\*  
Applicant Reference No.: DEN 105 Atty Docket No.: WLJ.075